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Determination of Kinetic Parameters from Steady-State Microdisk Voltammograms

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Equations are derived for the voltammetric response of an irreversible system in the steady-state regime at a small electrode. Voltammetric data for oxidation of Fe(II) in 0.1 M H₂SO₄ at circular platinum electrodes of radius 5 and 12.5 μ m are analyzed by a semilogarithmic technique and by reciprocal plots analogous to treatments of rotating disk voltammograms. The resulting values of kinetic parameters are standard rate constant $k_s = (1.5 \pm 0.2) \times 10^{-3}$ cm/s and anodic transfer coefficient $(1 - \alpha) = 0.67 \pm 0.01$. This technique compares favorably with others for determining rate parameters in the same range by virtue of technical and mathematical simplicity.

Very small electrodes have received increasing use in kinetic studies. Bindra et al. applied concepts of nonplanar diffusion to distributions of mercury droplets on carbon to measure the rate of the reaction $\text{Hg}_2^{2+} + 2e^- = 2\text{Hg}$.^{1,2} Howell and Wightman have made use of the low iR drop at small electrodes to carry out cyclic voltammetry at very high scan rates ($\sim 10^3$ V/s). Under these conditions standard heterogeneous rate constants with values exceeding 1 cm/s can be determined.³ Scharifker and Hills⁴ have made use of the increased rate of mass transport at smaller electrodes in studies of the kinetics of the reaction $\text{Fe}(\text{CN})_6^{3-} + e^- = \text{Fe}(\text{CN})_6^{4-}$. Russell et al.⁵ have employed thin rings for kinetic studies.

Consider the limiting processes which control voltammetric current. In the absence of chemical complications both mass transport and charge transfer may affect the current. In order to determine the charge-transfer rate from current measurements, the rate of charge transfer must be sufficiently small in comparison with the rate of mass transport. For example, if mass transport occurs by diffusion with diffusion coefficient D over diffusion layer

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thickness δ , then generally values of $k_h < D/\delta$ can be determined, where k_h is the forward rate constant for the heterogeneous charge-transfer process.

Suppose that the voltammetric experiment is chronoamperometry at a large planar electrode in quiet solution. Then $\delta = (\pi Dt)^{1/2}$, and for $D = 9 \times 10^{-6} \text{ cm}^2/\text{s}$, $k_h < 2 \times 10^{-3}/t^{1/2}$. For a routine experiment $t = 20 \text{ ms}$ and $k_h < 0.01 \text{ cm/s}$, whereas for a technically demanding experiment $t = 200 \mu\text{s}$ and $k_h < 0.1 \text{ cm/s}$. Corresponding scan rates for cyclic voltammetry are 1 and 130 V/s, respectively, and corresponding rotation rates in rotating disk voltammetry are 430 and 43 000 rpm, respectively.

Now consider a similar experiment at a small electrode for which nonplanar diffusion predominates. For the sake of simplicity we describe the diffusion-limited current, i_L , at a spherical electrode of radius r_0

$$i_L = nFAD_0C_0^0(1/(\pi D_0 t)^{1/2} + 1/r_0) \quad (1)$$

where n is the number of electrons transferred in the reduction of substance O at bulk concentration C_0^0 , D_0 is the diffusion coefficient of O, A is the electrode area, and F is the value of the Faraday. The radius r_0 formally corresponds to the diffusion layer thickness for spherical diffusion, and at sufficiently long times a steady state is reached. Again assuming $D_0 = 9 \times 10^{-6} \text{ cm}^2/\text{s}$, the times 20 ms and 200 μs correspond to electrode radii of 7.5 and 0.75 μm , respectively. At the present state of technology, it is possible routinely to make robust electrodes with sizes on the order of 3 μm . Thus, one can use these electrodes to enhance mass transport and therefore to determine rate constants by using very simple experiments on relatively long time scales and employing very simple analysis of data.

Specifically, this approach makes it possible to determine rate constants without special expertise, instruments, or mathematical skills and thus makes these measurements readily accessible as tools for characterizing chemical systems. Such simple suggestions often conceal problems with accuracy or precision of data or employ mathematical techniques for analysis which are dangerously self-justifying. To our knowledge there is no published example which presents the equations on which this method is based and subjects suitable data to alternative ways of analysis. In the present paper we derive equations for two ways of analyzing voltammetric data obtained at small electrodes and illustrate how to verify that the voltammograms are in the appropriate steady-state regime. These procedures are applied to determine the rate of oxidation of Fe(II) in 0.1 M H_2SO_4 at platinum microdisk electrodes. This disk geometry provides a surface which can be polished and has been described theoretically for reversible systems.⁵ The Fe(II)/Fe(III) system has been studied previously, and values of the rate parameters are available.⁷⁻⁹

Experimental Section

Staircase voltammetric measurements were carried out by using a three-electrode system with a platinum microdisk, saturated calomel (SCE), and Pt wire as working, reference, and auxiliary electrodes, respectively. An EG&G PARC 273 potentiostat was used as the source of applied potential. A Keithley 427 current amplifier connected to the auxiliary input of the PARC 273 was used to measure the currents. These two devices were controlled by a PDP 8/e minicomputer. Staircase scans were of 4-mV step height with varied step width. Two Pt microdisk electrodes of 25- and 10- μm diameters were used. They were made by first sealing AESAR Johnson Matthey (25 μm) and Goodfellow (10 μm) wires under vacuum into small 1- μL glass capillaries (Drummond Scientific). Electrical connection was made by bonding to a larger wire with silver epoxy. The cross section of the sealed Pt was polished gradually, starting with a CarbiMet paper disk and continuing with alumina powder going down from 1 μm (particle size) through 0.5 μm to 0.05 μm . Then the

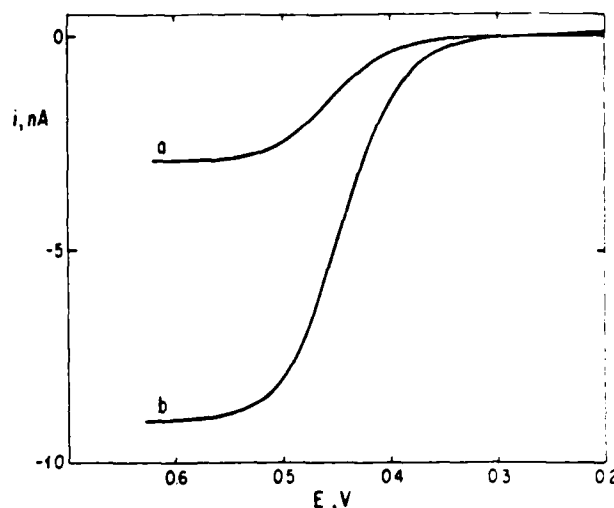


Figure 1. Steady-state voltammograms for oxidation of 2.5 mM Fe(II) and 0.1 M H_2SO_4 obtained with circular Pt electrodes. r_0 (μm) = (a) 5 and (b) 12.5.

electrodes were rinsed with water in an ultrasonic bath, and the quality of the surface was checked before each series of experiments by using an inverted (Leitz DIAVERT) light microscope with 500 \times magnification. Examples of typical steady-state cyclic voltammograms for the oxidation of Fe(II) are shown in Figure 1. Note especially that the voltammograms are substantially free of background current.

The characteristic parameters of voltammetric curves (i.e., limiting current, half-wave potential, and slope of the semilogarithmic dependence $\log(i_L - i)/i$ vs E) were determined by three-line graphical analysis with the aid of the computer.

The formal potential of the system Fe(II)/Fe(III) in 0.1 M H_2SO_4 was determined by potentiometric measurement using a large Pt wire indicator electrode and SCE reference electrode. The value obtained of $E^{\circ'} = +0.435 \text{ V}$ was then used to calculate the reversible half-wave potential (eq 14) assuming $D_R/D_O = 1.21$.⁷ The resulting value, $E_{1/2}^{\circ} = +0.440 \text{ V}$, was used in all calculations.

All reagents were of analytical grade. Ferrous sulfate solutions in 0.1 M H_2SO_4 were prepared freshly each time and purged with argon before measurements.

Results and Discussion

Theory. We begin by deriving equations which describe the voltammograms. In the case of a quasi-reversible reaction



the total current is given by

$$i = nFA[k_h C_O(0) - k_{-h} C_R(0)] \quad (3)$$

where $C_O(0)$ and $C_R(0)$ are concentrations at the electrode surface, while k_h and k_{-h} are cathodic and anodic heterogeneous rate constants for the cathodic and anodic process, respectively, at some given potential E . By eq 3, we are assuming uniform current density and surface concentrations. When the electrode is small and the step width is relatively long (i.e., $r_0/(Dt)^{1/2} \ll 1$, where r_0 is the radius of the disk), steady-state current-potential curves are obtained with the limiting current equal to

$$-i_L = 4nFD_R r_0 C_R^0 \quad (4)$$

assuming that the reduced form only is present initially in the solution. Using eq 4 and assuming a linear concentration profile in the diffusion layer, we may express $C_R(0)$ and $C_O(0)$ as

$$-C_R(0) = (i_L - i)/4nFD_R r_0 \quad (5)$$

$$-C_O(0) = i/4nFD_O r_0 \quad (6)$$

The linear assumption is a good one based on the following ar-

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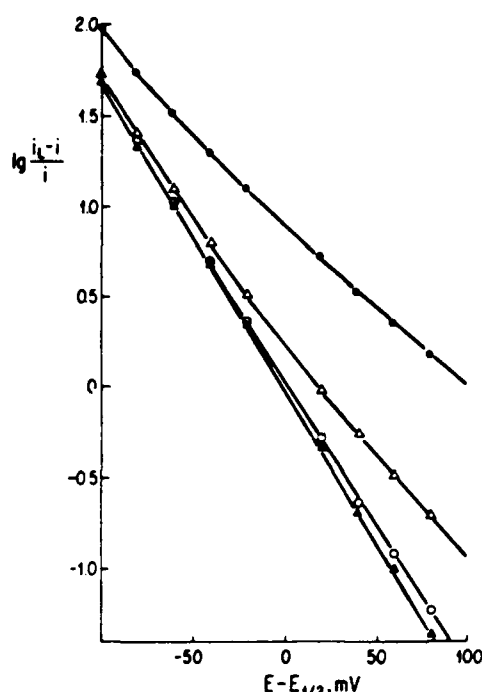


Figure 2. Calculated dependence of $\log [(i_L - i)/i]$ on $(E - E_{1/2})$ for steady-state microelectrode voltammograms. $k_s = 10^{-2}$ cm/s, $D_R = 7 \times 10^{-6}$ cm²/s; r_0 (cm) = Δ , 10^{-2} (O), 10^{-3} (Δ), and 10^{-4} (\bullet).

gument. The analogous problem for a sphere is readily solved exactly.¹⁰ With the restriction that $r_0/(Dt)^{1/2} \ll 1$, the solutions for concentration profiles at a sphere become identical with eq 5 and 6 when one employs in them the formula for the area of a disk. Using eq 5 and 6, $A = \pi r_0^2$ and the dependence of k_b and k_{bb} on potential in the classical form

$$k_b = k_s \exp[-\alpha n f (E - E^{\circ})] \quad (7)$$

$$k_{bb} = k_s \exp[(1 - \alpha) n f (E - E^{\circ})] \quad (8)$$

where k_s is the standard heterogeneous rate constant, α is the transfer coefficient of the cathodic reaction, and $f = F/RT = 38.9$ V⁻¹ at 25 °C, one obtains

$$(4D_R/\pi k_s r_0) \exp[-(1 - \alpha) n f (E - E^{\circ})] = (i_L - i)/i - (D_R/D_O) \exp[-n f (E - E^{\circ})] \quad (9)$$

For a reversible reaction one can use the Nernst equation and eq 5 and 6 to obtain the current-potential dependence

$$E = E^{\circ} + (1/nf) \ln (D_R/D_O) + (1/nf) \ln [f/(i_L - i)] \quad (10)$$

where f is the reversible current at potential E . Thus, the last term in eq 9 equals $(i_L - f)/f$, and consequently eq 9 can be written as

$$(4D_R/\pi k_s r_0) \exp[-(1 - \alpha) n f (E - E^{\circ})] = (i_L - i)/i - (i_L - f)/f \quad (11)$$

Here f is the calculated reversible current and i the measured current for the kinetically controlled process at potential E .

Equation 11 is appealing, for it emphasizes the point that the quality of determination of k_s and α depends on the difference between the experimental system and a reversible system. For sufficiently large k_s or sufficiently positive values of E , the right-hand side of eq 11 is zero. On the other hand, when k_s is small the last term of the right-hand side of eq 11 is negligible at potentials for which i has a measurable value. Equation 11 has a form similar to that of an equation proposed earlier by

TABLE I: Experimental Limiting Currents with Values Corrected for Deviation from Steady-State Behavior^a

V , V/min	i_L , nA	p	$(i_L)_{ss}$, nA
4	3.087	0.327	2.94
2	3.073	0.232	2.97
1	3.032	0.164	2.96
0.5	2.958	0.116	2.91
0.2	2.825	0.073	2.80

^a 2.5 mM FeSO₄ in 0.1 M H₂SO₄, $r_0 = 5 \mu\text{m}$. ^b Calculated from $i = \Delta E_s/t$ where ΔE_s is the step height (4 mV) and t the step width. ^c Experimental value. ^d $p = (n/r_0^2 v/D)^{1/2}$. ^e $(i_L)_{ss} = i_L/[0.34 \exp(-0.66p) + 0.66 + 0.351p]$ from ref 10.

Malyszko¹¹ for calculation of kinetic parameters from rotating disk voltammograms.

The effects of slow charge transfer and of electrode size on the current-potential are illustrated by plots of $\log [(i_L - i)/i]$ vs $E - E_{1/2}$ calculated from eq 11 and displayed in Figure 2. For large values of r_0 the reaction behaves reversibly, so the plot is linear with the slope predicted by eq 10. But for decreasing r_0 , mass transport is enhanced and charge transfer increasingly limits the current, which shifts the apparent half-wave potential to more positive values (for oxidations) and decreases the slope and linearity of the plot.

Equation 11 may be used in two ways for determining the standard rate constant, k_s .

The first method is based on the logarithmic form of eq 11

$$E - E^{\circ} = [1/(1 - \alpha)nf] \ln (4D_R/\pi k_s r_0) - [1/(1 - \alpha)nf] \ln [(i_L - i)/i - (i_L - f)/f] \quad (12)$$

For a given value of r_0 the first term of the right-hand side of eq 12 is constant, so a plot of $\ln [(i_L - i)/i - (i_L - f)/f]$ vs $(E - E^{\circ})$ should be linear with a slope equal to $1/(1 - \alpha)nf$.

In the determination of the rate constant, $(i_L - f)/f$ is calculated from eq 10 assuming that either E° or

$$E_{1/2} = E^{\circ} + (1/nf) \ln (D_R/D_O) \quad (13)$$

is known, while $(i_L - i)/i$ is taken from the experimental steady-state current-potential curves. For $(E - E^{\circ}) = 0$ the right-hand terms of eq 12 are equal, and thus knowing the value of $[1/(1 - \alpha)nf] \ln (4D_R/\pi k_s r_0)$, one may easily calculate the standard rate constant, assuming r_0 and D_R are known. The value of $1/(1 - \alpha)nf$ equals the slope of the plot of $\ln [(i_L - i)/i - (i_L - f)/f]$ vs $(E - E^{\circ})$.

In the second method of calculation eq 11 is combined with eq 8 to give

$$i_L/i = 4D_R/\pi k_{bb} r_0 + i_L/f \quad (14)$$

Now experimental values of i_L/i should be plotted vs $1/r_0$. This dependence should be linear with a slope $4D_R/\pi k_{bb}$ which depends on the rate constant. By extrapolating the dependence to $1/r_0 = 0$, one can obtain i_L/f which can be calculated independently from eq 10. By constructing plots of i_L/i vs $1/r_0$ for different potentials, one gets a set of k_{bb} values. The plot of $\ln k_{bb}$ vs $(E - E^{\circ})$ should be linear with a slope equal to $1/(1 - \alpha)nf$. This method of analysis is similar to that used in rotating disk voltammetry where the square root of the angular velocity is analogous to r_0 .

It should be mentioned that the above considerations are valid only for systems where reactant and product are both soluble in the solution phase.

Before calculating rate constants from experimental data, it is necessary to check whether steady-state assumptions are fulfilled under the experimental conditions. To do that, the theory elaborated by Aoki et al.¹² is used. Using the electrode with 5- μm radius, even at the scan rate 4 V/min, the measured current deviates only several percent from the steady-state one. In Table I are given the measured values of i_L and the values corrected by

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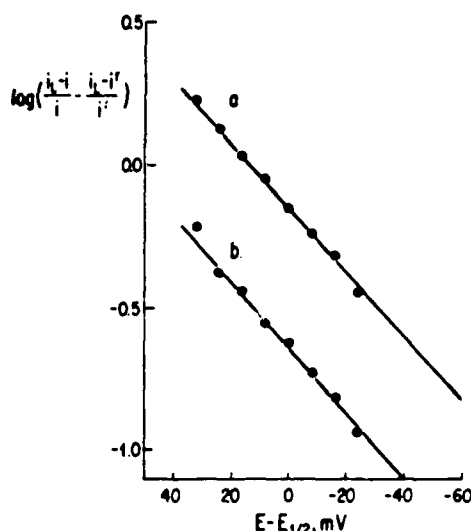


Figure 3. Dependence of $\log [(i_L - i)/i - (i_L - i')/i']$ on $(E - E_{1/2})$ calculated from voltammograms recorded for oxidation of 2.5 mM Fe(II) in 0.1 M H_2SO_4 . r_0 (μm) = (a) 5 and (b) 12.5.

dividing by the ratio of calculated currents for the given p value and the steady-state value (eq 4). The quantity p is the dimensionless electrode radius given by $p = (\pi r_0^2 \nu / D_R)^{1/2}$, and the value of $i_L(p)$ is calculated from eq 10 of ref 10. The resulting value of $(i_L)_\infty$ is constant and equal to 2.92 nA. This value seems to be reasonable since the diffusion coefficient value of Fe(II) calculated from this current via eq 4 is equal $6.02 \times 10^{-6} \text{ cm}^2/\text{s}$. Similar calculations show that when the larger electrode ($r_0 = 12.5 \mu\text{m}$) is used at scan rates 0.5 and 0.2 V/min, experimental currents are also not much different from the steady-state ones. In the calculation of rate constants only such current-potential dependencies were considered for which steady-state conditions were fulfilled within 4%.

Both of the methods suggested above for calculating k_s were employed. In Figure 3 are shown the plots of $\log [(i_L - i)/i - (i_L - i')/i']$ vs $(E - E_{1/2})$ (eq 12) obtained with 5- μm (curve a) and 12.5- μm (curve b) electrodes. Both plots are linear, and the slopes of 89 (a) and 87 mV (b) lead to the value 0.67 for the anodic transfer coefficient, $(1 - \alpha)$.

From the value of $\log [(i_L - i)/i - (i_L - i')/i']$ at $E = E^\circ$ the standard rate constant was found to be $1.15 \times 10^{-2} \text{ cm/s}$, using D_R given above. Similar analysis of a number of experimental voltammograms obtained with the 5- μm -radius electrode led to the average value of $k_s = 1.2 \times 10^{-2} \text{ cm/s}$ and $(1 - \alpha) = 0.68$. When the 12.5- μm -radius electrode was used, the deviation from reversibility was lower. The analysis of the current-potential curves recorded in a regime near to steady-state conditions (within 7%) gave values in the range 0.66–0.68 for $(1 - \alpha)$, while k_s values were slightly higher.

The second method of analysis based on eq 14 was used also. The results of this analysis for different potentials of the microdisk electrode are presented in Figure 4. Points corresponding to $1/r_0 = 0$ were calculated via eq 10. Two other sets of points represent the results obtained with 5- and 12.5- μm -radius electrodes at different potentials. At more anodic potentials the results obey fairly well the linear dependence predicted by eq 14. Also, the decrease of the slope of these lines with more positive potential is expected, since the rate constant k_s is becoming larger.

The logarithms of the values of k_s calculated from these slopes are plotted versus $(E - E_{1/2})$ in Figure 5. A reasonably good straight line is obtained with a slope leading to the transfer coefficient equal to 0.68, in agreement with the previous value. The rate constant calculated from this plot is equal to $1.8 \times 10^{-2} \text{ cm/s}$.

Other measurements of this rate constant are a bit lower than this value.⁷⁻⁹ In HClO_4 solutions on platinum the rate constant does not depend on concentration of acid and is about 10^{-2} cm/s .⁷ In H_2SO_4 values in the range $(3-7) \times 10^{-3} \text{ cm/s}$ are reported,

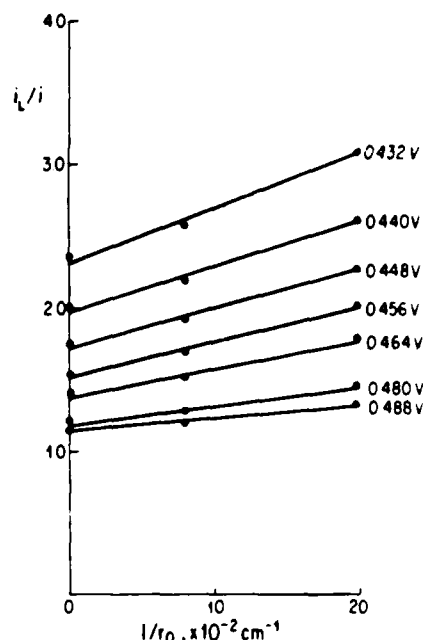


Figure 4. Dependence of (i_L/i) on $(1/r_0)$ for oxidation of 2.5 mM Fe(II) in 0.1 M H_2SO_4 at the potentials shown.

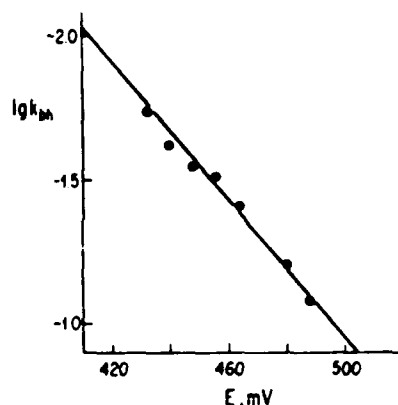


Figure 5. Dependence of $\log k_s$ on potential for oxidation of Fe(II) in 0.1 M H_2SO_4 . From the slopes of Figure 4.

but the value $1 \times 10^{-2} \text{ cm/s}$ is reported on gold. Values of the transfer coefficient are more variable. Most of the values reported for the cathodic transfer coefficient, α , are significantly greater than the value of 0.33 determined here. However, the values 0.42 and 0.46 (Pt, 0.1 M H_2SO_4) are quoted by Heusler.⁷ It must also be emphasized that the mechanism of this reaction is not well-understood, so that it is not surprising that rate data obtained under different conditions and analyzed according to the simple model of eq 3 yield a range of values for the rate parameters.

In the present treatment, deviations from steady-state conditions are interpreted as an increased rate of charge transfer. We have shown above (cf. Table I) how to calculate the percentage deviation from steady-state behavior based on the value of p . One can also use the value of p to estimate the shift in $E_{1/2}$ value due to departure from exact steady-state conditions.¹² This shift, $\Delta E_{1/2}$, establishes an upper limit for the resulting error in k_s , Δk_s , given by $\ln [(k_s + \Delta k_s)/k_s] = \eta/\Delta E_{1/2}$. In the present case, for example, a 2% deviation from steady state ($i_L/(i_L)_\infty = 1.02$) corresponds to $p = 0.16$ ($r_0 = 5 \mu\text{m}$ at $\nu = 1 \text{ V/min}$) and a negative shift in $E_{1/2}$ of 2.4 mV, so the value of k_s derived from the foregoing treatment would be at most 10% high. Typically, experimental errors in the potential are of this order.

Estimating the effect of transient current on the derived value of α is less straightforward, because the equations describing the shape of the voltammogram are quite complex. For the analogous

rotating disk case,¹³ numerical results have been obtained over a range of rotation rates, scan rates, and kinetic parameters. These suggest that for S-shaped (rather than peak-shaped) voltammograms, i.e., for $p \leq 1.6$, and for totally irreversible reactions, the shape of the voltammogram does not change with changes in p . The maximum value of p used here was 0.45, and for most of the data, $p \leq 0.28$. Furthermore, there is no trend in the derived value of $(1 - \alpha)$ with changes in p over this range.

We conclude that for voltammograms with only modest contribution of transient current ($\leq 5\%$) the systematic error introduced by treating the voltammograms as steady-state ones is not larger than the usual experimental errors.

Finally, we examine the reasonableness of the assumption that the current density is uniform. In 0.1 M H_2SO_4 , the specific conductance, κ , is ca. $0.04 \text{ ohm}^{-1} \text{ cm}^{-1}$ and the currents are in the low nanoampere range. Thus, concentration and charge-transfer polarization should predominate over Ohmic polarization, and the distribution of current should be uniform. Quantitatively, deviations from uniformity should be negligible for $J, \Delta \ll 1$, where

J and Δ are normalized exchange current density and average current density, respectively:¹⁴ $J = i^0 z / r_0 / \kappa$; $\Delta = |i_{av}| z / r_0 / \kappa$. For the present case $z = 2$ and $J \leq 0.003$, $\Delta \leq 0.002$. We conclude that the assumption of uniform current density is reasonable.

The procedure is summarized as follows. Conditions of step height and step width (or scan rate) and electrode radius are sought for which S-shaped voltammograms are obtained, as illustrated in Figure 1. Data are obtained for a range of radii and step width (scan rate) to verify that the limiting current behaves according to theory and that the operating conditions are acceptably close to the steady state, as illustrated in Table 1. Voltammograms are then analyzed according to eq 12 (Figure 3) or eq 14 (Figures 4 and 5), making use of an independently measured value of $E'_{1/2}$ and the value of D obtained from the limiting steady-state current.

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Registry No. Fe, 7439-89-6; Pt, 7440-06-4; H_2SO_4 , 7664-93-9.

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